

Process for the production of polyurethane urea fibers by including a combination of polydimethylsiloxane, alkoxyated polydimethylsiloxane and a fatty acid salt in the spinning solution

5 The invention relates to a wet spinning or dry spinning process, especially a dry spinning process, for the production of polyurethane urea fibers, in which there are added to the polyurethane urea composition, prior to spinning, from 0.1 to 5 wt.% polydimethylsiloxane having a viscosity of from 2 to 20 cSt (25°C), from 0.1 to 5 wt.% alkoxyated polydimethylsiloxane having a number average molecular
10 weight of less than 30,000 g/mol. and a viscosity of from 10 to 5000 cSt (25°C), and from 0.01 to 3 wt.% of a fatty acid salt (wt.% based on the polyurethane urea fibers).

Background of the invention

Elastic polyurethane urea fibers are to be understood as being fibers which are
15 composed to the extent of at least 85 wt.% of segmented polyurethanes based on, for example, polyethers, polyesters and/or polycarbonates and aromatic and/or aliphatic diisocyanates. Polyurethane urea fibers are usually produced by spinning solutions in accordance with the melt spinning process, the wet spinning process or, preferably, the dry spinning process. Suitable solvents for the wet and dry spinning
20 process are polar solvents, e.g. dimethyl sulfoxide, dimethylformamide, N-methylpyrrolidone and, preferably, dimethylacetamide. Such spinning processes are described, for example, in Polyurethan-Elastomerfasern, H. Gall and M. Kausch in Kunststoff-Handbuch 7, Polyurethane, Ed.: G. Oertel, Carl Hanser Verlag Munich Vienna, 1993, pages 679 to 694.

25 Polyurethane urea fibers exhibit outstanding elasticity and pronounced extensibility in combination with high restoring forces. Owing to that outstanding combination of properties, they are widely used in the clothing sector. The most important field of use of such fibers is the elasticizing function for linen, corsetry and sportswear, such
30 as, for example, bathing suits and bathing trunks, as well as use in garter welts for hosiery, socks, elastic bands or diapers.

The economy of the production of polyurethane urea fibers is determined in a decisive manner by the spinning process. In the dry spinning process, for example, the highly viscous spinning solution is fed to the heated spinning shaft, filtered and pressed through multihole nozzles, the solvent rapidly evaporating as a result of hot spinning air that is supplied. The finished individual filaments are bundled together in the spinning shaft – according to the desired denier – to form a yarn and bonded together by a twisting device to form a virtually monofilament thread. A finishing oil can be applied. The finished thread is finally wound onto bobbins. In that manner, a 480 dtex elastane thread, for example, can be produced from 36 individual filaments.

The economy of that polyurethane urea fiber production process is dependent in a decisive manner on the speed with which the thread is wound onto the bobbin. If that speed is high, the throughput of spinning solution per spinneret is also high. The spinning solution or additives contained therein should therefore be so selected that filters do not become blocked during the spinning process. If blocking nevertheless occurs, the spinning process must be interrupted. In such a case, the yield and the economy, associated therewith, is reduced. A second, equally important parameter in relation to the economy is the achievement of textile thread data at a constant level throughout the spinning process. If thread data change during the spinning process, polyurethane urea fibers that are not within the specification may be obtained. Products that do not comply with the specification are removed, and the economy is reduced.

The object of this invention is to permit the production of polyurethane urea fibers with constant textile thread data over the entire spinning process and with increased productivity.

Summary of the invention

It has been found, surprisingly, that this object can be achieved by adding to the solution of the polyurethane urea composition, prior to spinning, a mixture of from 0.1 to 5 wt.% polydimethylsiloxane (PDMS) having a viscosity of from 2 to 20 cSt (25°C), from 0.1 to 5 wt.% alkoxyated polydimethylsiloxane having a molar mass
5 (number average) of less than 30,000 g/mol. and a viscosity of from 10 to 5000 cSt (25°C), and from 0.01 to 3 wt.% fatty acid salt (wt.% based on the polyurethane urea fibers) and then carrying out the spinning process.

The inclusion of pure polydimethylsiloxane in polyurethane urea fiber spinning
10 solutions is known in principle. It is described, for example, in DE-A-3 912 510, which describes the production of elastanes by a special spinning process with the introduction of superheated steam to produce coarse denier elastane fibers. Silicone oils are mentioned therein among other possible additives as flow improvers. US patent specification 4 973 647 also mentions the inclusion of silicone oil in the
15 spinning solution. Neither document makes any reference to the inclusion of a special combination of oils having particular properties in the spinning solution.

The inclusion of amylsiloxane-modified polydimethylsiloxane oils in the spinning solution, which is not the subject of the invention, is also known from specification
20 DE-AS 1 469 452.

The inclusion in the spinning solution of a combination of polydimethylsiloxane having a viscosity of from 50 to 300 cSt (25°C) and ethoxylated polydimethylsiloxane having a viscosity of from 20 to 150 cSt (25°C) in order to
25 produce polyurethane urea fibers is mentioned in specification EP 643 159. However, the inclusion of the mixture recommended in that application in the spinning solution leads to a reduction in the effectiveness of the anti-adhesion agent, e.g. magnesium stearate. In order to establish the necessary adhesion for the processing of the polyurethane urea fibers to, for example, textile fabrics, it is
30 necessary to include an additional, i.e. an increased, amount of anti-adhesion agent in the fiber spinning solution. An increased amount of anti-adhesion agent, e.g.

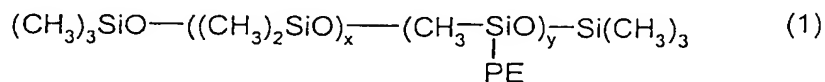
magnesium stearate, leads to a shortening of the useful lives of filters in the spinning process owing to increased blocking. The spinning process is interrupted, with a loss of yield, for the necessary premature filter exchange. Furthermore, the mixture recommended in the application can, in dependence on time and temperature, lead to agglomeration of magnesium stearate before addition to the polyurethane urea composition fed to the spinning process. As a result of the agglomerates that form over time, the effectiveness of magnesium stearate as an anti-adhesion agent can change. As the spinning process continues, textile data, e.g. adhesion, can change over time. Polyurethane urea fibers that are not within the specification are then removed in a complex operation, with a reduction in yield. That publication makes no reference to the fact that the viscosity of the polydimethylsiloxane used must not be below 50 cSt (25°C). By the inclusion according to the invention of a mixture of polydimethylsiloxane (PDMS) having a viscosity of from 2 to 20 cSt (25°C), alkoxyated polydimethylsiloxane having a viscosity of from 10 to 5000 cSt (25°C) and a fatty acid salt in the spinning solution, the above-mentioned disadvantages relating to the economy of the polyurethane urea fiber production do not occur.

The application of mixtures of polydimethylsiloxane and polyether-modified PDMS to the finished spun elastane threads by dipping, spraying or by means of a roller is likewise known (see in this respect JP 57 128 276 or JP 03 146 774). The application of such finishing oils serves to improve the take-off properties of the elastane fibers in warping and knitting processes. There is no mention in those specifications of the inclusion of the mixture in the spinning solution. Likewise, there is no indication that mixtures, especially those containing the compositions according to the invention, included in the elastane fiber spinning solution can lead to an improvement in the productivity of the spinning process.

30 Detailed description

The invention provides polyurethane urea fibers, characterised in that they are comprised of

- 5 A) from 99.7 to 65 wt.%, especially from 99.5 to 80 wt.%, particularly preferably from 99 to 85 wt.%, polyurethane urea polymer,
- B) from 0.1 to 5 wt.%, especially from 0.2 to 3 wt.%, particularly preferably from 0.3 to 2 wt.%, polydimethylsiloxane having a viscosity of from 2 to 20 cSt (25°C),
- 10 C) from 0.1 to 5 wt.%, especially from 0.2 to 3 wt.%, particularly preferably from 0.3 to 2 wt.%, alkoxyated polydimethylsiloxane (PDMS) corresponding to the general formula (1)



15 wherein

PE is the monovalent radical $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}(\text{eo}_v/\text{po}_w)_m\text{Z}$,

eo represents ethylene oxide,

20

po represents propylene oxide and

Z is either hydrogen or a C_1 - C_6 -alkyl radical,

25 v and w are integers greater than or equal to 0, wherein v and w are not simultaneously 0,

x, y and m are integers greater than or equal to 1, which are preferably so selected that the number average molecular weight (number average) of formula (1) does not exceed 30,000 g/mol. and the viscosity of C) is from 10 to 5000 cSt (25°C),

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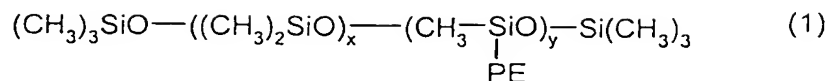
D) from 0.01 to 3 wt.%, preferably from 0.05 to 2 wt.%, particularly preferably from 0.1 to 1.5 wt.%, of a metal salt of a saturated or unsaturated, mono- or bi-functional C₆-C₃₀ fatty acid, wherein the metal is a metal selected from the first, second or third main group of the periodic system, or is zinc,
10 and

E) from 0 to 20 wt.%, especially from 0 to 15 wt.%, additives.

The invention also provides a process for the production of improved polyurethane urea fibers by the dry spinning or wet spinning process, preferably by the dry
15 spinning process, by preparing the spinning solution, spinning the spinning solution using a spinneret, forming threads beneath the spinneret by removing the spinning solvent by drying or in a precipitation bath, finishing and winding the threads, which process is characterised in that the following components are added to the
20 polyurethane urea solution before the solution is spun to form polyurethane urea fibers:

B) from 0.1 to 5 wt.%, especially from 0.2 to 3 wt.%, particularly preferably from 0.3 to 2 wt.%, polydimethylsiloxane having a viscosity of from 2 to
25 20 cSt (25°C),

C) from 0.1 to 5 wt.%, especially from 0.2 to 3 wt.%, particularly preferably from 0.3 to 2 wt.%, alkoxyated polydimethylsiloxane (PDMS) corresponding to the general formula (1)



wherein

PE is the monovalent radical $-CH_2-CH_2-CH_2-O(eo_v/poO_w)_mZ$,

eo represents ethylene oxide,

po represents propylene oxide and

Z is either hydrogen or a C_1-C_6 -alkyl radical,

v and w are integers greater than or equal to 0, wherein v and w are not simultaneously 0,

x, y and m are integers greater than or equal to 1, which are preferably so selected that the molecular weight (number average) of formula (1) does not exceed 30,000 g/mol. and the viscosity of component C) is from 10 to 5000 cSt (25°C),

and

D) from 0.01 to 3 wt.%, preferably from 0.05 to 2 wt.%, particularly preferably from 0.1 to 1.5 wt.%, of a metal salt of a saturated or unsaturated, mono- or bi-functional C_6-C_{30} fatty acid, wherein the metal is a metal selected from the first, second or third main group of the periodic system, or is zinc.

Preference is given also to fibers obtainable by the process according to the invention.

The polyurethane urea fibers according to the invention contain the polydimethylsiloxanes, alkoxyated polydimethylsiloxanes and fatty acid salts mentioned under B), C) and D) in finely dispersed form (domains) or in dissolved form. The domains in the polyurethane urea fibers have a length in the longitudinal direction of the filaments of especially less than 24 μm , preferably less than 18 μm and particularly preferably less than 15 μm . The domains in the transverse direction of the filaments have a size of especially less than 6 μm , preferably less than 5 μm and particularly preferably less than 4 μm . The polyurethane urea fibers according to the invention consist of segmented polyurethane urea polymers. The polymers have a segment structure, that is to say they consist of "crystalline" and "amorphous" blocks (so-called hard segments and soft segments).

The polyurethane urea composition and the polyurethane urea fibers can be produced especially from a linear homo- or co-polymer each having a hydroxy group at the end of the molecule and a molecular weight (number average) of from 600 to 6000 g/mol., such as polyether diols, polyester diols, polyester amide diols, polycarbonate diols, or of a mixture or of copolymers of that group. They are also based on organic diisocyanates, with which the polymeric diols are reacted to form terminally isocyanate-functional prepolymers, and diamines or mixtures of different diamines as chain extenders, with which the terminally isocyanate-functional prepolymers are reacted to form high polymers.

The described reactions are usually carried out in an inert polar solvent, such as dimethylacetamide, dimethylformamide, N-methylpyrrolidone or the like. The preparation of terminally isocyanate-functional prepolymers can also be carried out in the melt.

For the preparation of terminal isocyanate-functional prepolymers it is also possible to use polyester diols and/or polyether diols in combination with diols that contain tertiary amino groups. N-Alkyl-N,N-bis-hydroxyalkylamines, for example, are especially suitable. Examples of components which may be mentioned here include:

4-tert.-butyl-3-aza-2,6-heptanediol, 4-methyl-4-aza-2,6-heptanediol, 3-ethyl-3-aza-1,5-pentanediol, 2-ethyl-2-dimethylaminomethyl-1,3-propanediol, 4-tert.-pentyl-4-aza-2,6-heptanediol, 3-cyclohexyl-3-aza-1,5-pentanediol, 3-methyl-3-aza-1,5-pentanediol, 3-tert.-butylmethyl-3-aza-1,5-pentanediol and 3-tert.-pentyl-3-aza-1,5-pentanediol.

Examples of organic diisocyanates include 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate and 4,4'-diphenylmethane diisocyanate. Examples of diamines include ethylenediamine, 1,2-propanediamine, 2-methyl-1,5-diaminopentane, isophoronediamine, 1,3-diaminocyclohexane, 1-methyl-2,4-diaminocyclohexane and 1,2-diaminocyclohexane. The desired molecular weight can be established by using a small amount of monoamines as chain terminator, e.g. diethylamine, dibutylamine or ethanolamine, during the chain extension. The chain extension itself can be carried out using CO₂ as retarding agent.

The polyurethane urea fibers can be prepared according to processes which are known in principle, such as, for example, according to those described in specifications US 2 929 804, US 3 097 192, US 3 428 711, US 3 553 290 and US 3 555 115 and in specification WO 9 309 174.

The polyurethane urea fibers according to the invention can be used in the production of elastic fabrics, knitted goods, hosiery and other textile products. The invention also provides that use.

In accordance with the process according to the invention, the polydimethylsiloxane having a viscosity of from 2 to 20 cSt (25°C) is introduced in a concentration of from 0.1 to 5 wt.%, the alkoxyated polydimethylsiloxane having a molar mass (number average) of less than 30,000 g/mol. and a viscosity of from 10 to 5000 cSt (25°C) is introduced in a concentration of from 0.1 to 5.0 wt.%, and the metal salt of a fatty acid is introduced in a concentration of from 0.01 to 3.0 wt.%, based on the

polyurethane urea fibers. The weight ratio of polydimethylsiloxane to alkoxylated polydimethylsiloxane in the finished phase is preferably 2:1 to 1:2 after adjustment of the sub-components B), C) and D). The weight ratio of polydimethylsiloxane to fatty acid salt in the finished phase is preferably 2:1 to 1:2. The data relating to concentrations mean the content of oil or fatty acid salt in the finished spun elastane filament.

The oils and the fatty acid salt can be added to the polyurethane urea composition before the production of polyurethane urea fibers at any desired point in the processing of the composition. For example, the oils and the fatty acid salt can be added in the form of a solution to a solution, dispersion or suspension of other additives. During processing to fibers, they can then be mixed with or injected into the polymer solution upstream relative to the fiber spinnerets.

The incorporation of the oils and of the fatty acid salt into the polyurethane urea composition is preferably carried out with the aid of a stock formulation, in which the oils and the fatty acid salt are dispersed, together with other spinning auxiliaries, in the solvent, e.g. dimethylacetamide. The stock formulation is then mixed with the spinning solution by means of a dynamic or static mixer. The concentration of the two silicone oils and of the fatty acid salt together in the common stock formulation solution is preferably from 10 to 25 wt.%.

The polyurethane urea fibers are then produced from the resulting spinning solution by the wet spinning or dry spinning process, preferably by the dry spinning process. Fibers produced by the process preferably have an individual denier of from 10 to 1280 dtex. The individual deniers can be produced in the form of monofilaments or from multifilament fibers consisting of, for example, from 2 to 200 coalesced individual capillaries. After leaving the spinning shaft, the fibers may be provided with an external finish.

Suitable fatty acid salts D) within the scope of the invention are those whose metal is a metal of the first to third main groups of the periodic system, or is zinc. The fatty acids are saturated or unsaturated, are composed of at least six and not more than 30 carbon atoms and are mono- or bi-functional. The fatty acid salts according to the invention are especially lithium, magnesium, calcium, aluminum and zinc salts of oleic, palmitic or stearic acid, particularly preferably magnesium stearate, calcium stearate or aluminum stearate.

The polyurethane urea compositions or polyurethane urea fibers according to the invention produced therefrom can contain as additives E) delustering agents, fillers, antioxidants, dyes, pigments, staining agents, and stabilizers against heat, light, UV radiation, chlorine-containing water, chemical fiber-cleaning agents, especially chlorinated hydrocarbons, and against vapors.

Examples of antioxidants and stabilizers against heat, light or UV radiation are stabilizers from the group of the sterically hindered phenols, HALS stabilizers (hindered amine light stabilizer), triazines, benzophenones and benzotriazoles. Examples of pigments and delustering agents are titanium dioxide, zinc oxide and barium sulfate. Examples of dyes are acid dyes, dispersion and pigment dyes and optical brightening agents. Examples of stabilizers against degradation of the fibers by chlorine or chlorine-containing water are zinc oxide, magnesium oxide, calcium-magnesium carbonates, calcium-magnesium hydroxy carbonates or magnesium-aluminum hydroxycarbonates, especially hydrotalcite. The mentioned stabilizers can also be used in the form of mixtures and contain an organic or inorganic coating agent.

The invention is explained in greater detail below by means of Examples, which do not, however, represent any limitation of the invention.

Examples:

The polyurethane urea solution used for the following Examples is prepared in accordance with the following procedure:

5

In all the Examples, polyurethane urea compositions are prepared from a polyester diol having a molecular weight (number average) of 2000 g/mol., which consists of adipic acid, hexanediol and neopentyl glycol and has been masked with methylene bis(4-phenyldiisocyanate) (MDI, Bayer AG) and then chain-extended with a mixture of ethylenediamine (EDA) and diethylamine (DEA).

10

The polyurethane urea compositions for each of the Examples are prepared by the same process.

15

For the preparation of the polyurethane urea composition, 50 wt.% polyester diol having a molecular weight (number average) of 2000 g/mol. are mixed with 1 wt.% 4-methyl-4-aza-2,6-heptanediol, and 36.2 wt.% dimethylacetamide (DMAC) and 12.8 wt.% MDI at 25°C, heated to 50°C and maintained at that temperature for 110 minutes in order to obtain an isocyanate-masked polymer having an NCO content of 2.65 % NCO.

20

After cooling to a temperature of 25°C, 100 parts by weight of the masked polymer are rapidly mixed into a solution of 1.32 parts by weight of EDA and 0.04 parts by weight of DEA in 187 parts of DMAC so that a polyurethane urea composition in DMAC having a solids content of 22 % is formed. By addition of hexamethylene diisocyanate (HDI, Bayer AG), the molecular weight of the polymer is adjusted to give a viscosity of 70 Pa*s (25°C).

25

Following the preparation of the polymers as described in the preceding section, a stock formulation of additives is added thereto. The stock formulation consists of 65.6 wt.% DMAC, 11.5 wt.% CYANOXTM 1790 ((1,3,5-tris(4-tert.-butyl-3-hydroxy-2,5-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, Cytec), 5.7

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wt.% TINUVINTM 622 (polymer having a molar mass of about 3500 g/mol., consisting of succinic acid and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, Ciba Geigy), 17.2 wt.% 22 % spinning solution and 0.001 wt.% of the dye MAKROVOEVIOLETTTM B (Bayer AG). The stock formulation is metered into the spinning solution in such a manner that the content of CYANOXTM 1790 is 1.0 wt.% and the content of TINUVINTM 622 is 0.5 wt.%, based on the total solids content in the polyurethane urea composition.

A second stock formulation, consisting of 31 wt.% titanium dioxide (TRONOXTM TiO₂ R-KB-3, Kerr-McGee Pigments GmbH & Co. KG), 44.5 wt.% dimethylacetamide and 24.5 wt.% 22 % spinning solution is added to the first spinning solution in such a manner that the titanium dioxide content in the finished thread is 0.05 wt.%, based on the finished polyurethane urea fibers.

Further stock formulations are then added to that spinning solution. They consist of 5.3 wt.% magnesium stearate (Peter Greven), 49.6 wt.% DMAC, 33.8 wt.% 22 % spinning solution, 6.0 wt.% polydimethylsiloxane and 5.3 wt.% SILWETTM L 7607 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, methyl-terminated, molecular weight 1000 g/mol., viscosity 50 cSt (25°C)), which are so chosen that the percentage contents indicated in Examples 1 to 3 are obtained in the finished fibers.

Example 1

Additive content in the finished polyurethane urea fibers:

0.28 wt.% magnesium stearate

0.28 wt.% SILWETTM L 7607

0.32 wt.% BAYSILONETM oil M 5 (polydimethylsiloxane GE Bayer Silicones, viscosity 5 cSt (25°C)).

Example 2

Additive content in the finished polyurethane urea fibers:

0.19 wt.% magnesium stearate

5 0.19 wt.% SILWETTM L 7607

0.22 wt.% BAYSILONETM oil M 5 (GE Bayer Silicones, viscosity 5 cSt (25°C)).

Example 3 (comparison)

10 Additive content in the finished polyurethane urea fibers:

0.28 wt.% magnesium stearate

0.28 wt.% SILWETTM L 7607

0.32 wt.% BAYSILONETM oil M 100 (GE Bayer Silicones, viscosity 100 cSt (25°C)).

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In Examples 1 to 3, the polyurethane urea composition is spun in a spinning apparatus typical for a dry spinning process to form filaments having a denier of 11 dtex, 4 individual filaments being combined to form coalesced filament yarns of 44 dtex and being wound at a take-off speed of 550 m/min.

20

The filaments so obtained are tested for their mechanical properties and characterised. To that end, the count-related strength (CS) and the elongation at break (EB) in particular are measured in accordance with DIN 53834 Part 1. For that purpose, tensile tests are carried out on elastane filament yarns in the air-conditioned state. To that end, the prepared test specimen is placed in a loop around the hook of the measuring head and placed round a 10 mm looping clamp with a pretensioning force of 0.001 cN/dtex. The clamped length is 200 mm overall. A small vane of aluminum foil is suspended precisely at the level of a light barrier. The slide travels at a rate of deformation of 400%/min (800 mm take off) until the thread breaks, and returns to its starting position again after the measurement. 20 measurements are carried out per test specimen.

25

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5 The adhesion of the thread to a bobbin is determined by first detaching the thread from the bobbin above the bobbin case with a weight of 500 g, except for 3 mm. A weight is then suspended from the thread and the weight at which the thread unrolls from the bobbin is determined. The adhesion so determined is a measure of the processability of the bobbins. If the adhesion is too high, processability to sheet-form textile products may be made more difficult owing to the tearing of threads. If the adhesion is too low, it is possible that, during the winding process in the dry spinning shaft or during further processing of the bobbin to textile fabrics, the thread
10 may fall off the bobbin, tear and accordingly not undergo further processing.

The optical uniformity is evaluated by the method described hereinbelow.

15 In a first step, 1340 threads of denier dtex 44 are warped with a preliminary draft of 156 % and a final draft of 40 % onto two sectional warp beams (SWBs) of an elastane warping machine (type DSE 50/30 from Karl Mayer, Oberhausen).

20 In a second step, an elastic warp-knitted fabric is produced from those sectional warp beams together with two SWBs of polyamide dtex 44/10 from Snia. A type HKS 2/E 32 warp loom (Karl Mayer, Oberhausen) is used as the warp knitting machine.

25 The warp-knitted fabrics so produced are then relaxed on a steaming table. In the further process, fixing with hot air is carried out in the non-prewashed state on a tenter frame for 40 seconds at 195°C and with an overfeed of 8 %. The fixing width is 100 cm.

30 In a separate pass through the tenter frame, the fixed fabric is wound cold onto perforated dyeing beams.

The fabric is dyed blue in a beam dyeing apparatus in accordance with the following formulation:

0.90 % TELONTM Lichtblau RR 182 % (Bayer AG; acid dye)

0.05 % TELONTM Echtorange AGT 200 % (Bayer AG; acid dye)

5 2.00 g/l sodium acetate

1.50 % LEVOGALTM FTS (Bayer AG; leveling agent) and

0.30 ml/l acetic acid.

10 Before all the auxiliaries are added, the closed apparatus is first filled with water with no circulation of liquor. The addition of the above-mentioned auxiliaries is carried out after the circulation pump has been switched on and the required pressure of 2.2 to 2.0 bar has been established. Heating of the liquor is carried out at 1°C per minute, the chosen liquor direction being outside/inside up to 80°C and the liquor being pumped from the inside outwards above 80°C. Once the required final
15 temperature of 98°C has been reached, the further treatment time is 60 minutes. Indirect cooling to 70°C is then carried out, followed by continuous rinsing by the supply of fresh cold water and, finally, rinsing once more with fresh water.

20 After dyeing, the dyeing beams with the wet fabric are delivered to the padding machine, passed through rinsing water during passage through the padding machine and uniformly squeezed dry.

25 Subsequent intermediate drying is carried out in a perforated cylinder drier at 120°C with a rate of travel of about 7 m/min. The fabric is folded flat on entering the perforated cylinder drier.

30 The intermediately dried fabric is finally tentered in a tenter frame at a temperature of 150°C and at a fabric speed of 10 m/min and with an overfeed of 5 %, resulting in a smooth finished fabric which is wound up on leaving the tenter frame.

Optical uniformity is evaluated by means of a visual inspection of the finished dyed fabrics both in transmitted light and in reflected light and is evaluated by means of a scale of ratings (test rating) which ranges from 1 to 9. For the polyurethane urea fibers dtex 44 described here, rating 4 represents a very uniform fabric, rating 5 still corresponds to good uniformity, rating 6 corresponds to satisfactory uniformity. If a fabric is rated 7, it can be used only for special purposes. Fabrics rated 8 and 9 are unsaleable.

Table 1 shows the determined filament properties and the test ratings for evaluation of the optical uniformity.

Table 1

Tabular comparison of the thread data and the test ratings for evaluating optical uniformity:

| Example number | Denier (dtex) | CS (cN/dtex) | EB (%) | Adhesion (cN) | <u>Test rating</u> |
|----------------|---------------|--------------|--------|---------------|--------------------|
| 1 | 43.6 | 1.24 | 417 | 0.05 | n.d. |
| 2 | 45.7 | 1.21 | 420 | 0.23 | 5.0 |
| 3 (comparison) | 45.2 | 1.21 | 402 | 0.23 | 5.0 |

CS: count-related strength, EB: elongation at break.

As the Examples show, the adhesion is clearly changed by the addition of a stock formulation based on BAYSILONETM oil M5 in comparison with one based on BAYSILONETM oil M100. Accordingly, the adhesion is considerably reduced by addition of a stock formulation based on BAYSILONETM oil M5 in comparison with BAYSILONETM oil M100. It can thus be demonstrated that the effectiveness of magnesium stearate as an anti-adhesion agent is clearly increased when a stock formulation based on BAYSILONETM oil M5 is used. In the case of the stock

formulation based on BAYSILONE™ oil M100, the effectiveness of magnesium stearate is reduced as a result of agglomerate formation. By reducing the inclusion of BAYSILONE™ oil M5 in the spinning solution, the adhesion can readily be adjusted to the level of the stock formulation based on BAYSILONE™ oil M100.

5 By including a stock formulation based on BAYSILONE™ oil M5 in the spinning solution, the useful life of filters in the spinning process can be lengthened and the productivity accordingly increased.

10 The count-related strength (CS) and the evaluation of optical uniformity are independent of the stock formulation and remain unchanged at a constant level.

In the series of tests for Examples 4 to 9, stock formulations were prepared with different polydimethylsiloxanes and alkoxyated polydimethylsiloxanes. The stock formulations consist of 5.3 wt.% magnesium stearate (Peter Greven), 49.6 wt.%
15 DMAC, 33.8 wt.% 30 % spinning solution, 6.0 wt.% polydimethylsiloxane and 5.3 wt.% alkoxyated polydimethylsiloxane.

The stock formulations are stored at 25°C and 50°C and their homogeneity is assessed immediately and after standing for 24 hours.

20 The assessment of the homogeneity of the stock formulations is shown in Table 2.

The 30 % spinning solution used to prepare the stock formulations is prepared from a polyether diol consisting of polytetrahydrofuran (PTHF, e.g. Terathane 2000 from
25 Du Pont) having an average molecular weight (number average) of 2000 g/mol.. The diol is masked with methylene bis(4-phenyldiisocyanate) (MDI, Bayer AG) at a molar ratio of 1 to 1.65 and then chain-extended with a mixture of ethylenediamine (EDA) and diethylamine (DEA) in a weight ratio of 97:3 in dimethylacetamide (DMAC). The ratio of the amount of chain extender and chain terminator to
30 unreacted isocyanate in the prepolymer is 1.075. The solids content of the resulting polyurethane urea solution is 30 wt.%.

A stock formulation of additives is then mixed with the polymer. That stock formulation consists of 62.7 wt.% dimethylacetamide (DMAC), 10.3 wt.% CYANOXTM 1790 ((1,3,5-tris(4-tert.-butyl-3-hydroxy-2,5-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, Cytec), 27.0 wt.% 30 % spinning solution and 0.001 wt.% of the dye MAKROLEXVIOLETTTM B (Bayer AG). The stock formulation is added to the polyurethane urea composition in such a manner that the content of CYANOXTM 1790 is 1.0 wt.%, based on the total solids content.

10 **Example 4**

5.3 wt.% magnesium stearate

6.0 wt.% BAYSILONETM oil M 3 (GE Bayer Silicones, viscosity 3 cSt (25°C))

15 5.3 wt.% SILWETTM L7607 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, methyl-terminated, molecular weight 1000 g/mol., viscosity 50 cSt (25°C)).

Example 5

20 5.3 wt.% magnesium stearate

6.0 wt.% BAYSILONETM oil M 5 (GE Bayer Silicones, viscosity 5 cSt (25°C))

5.3 wt.% SILWETTM L7607 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, methyl-terminated, molecular weight 1000 g/mol., viscosity 50 cSt (25°C)).

25

Example 6 (comparison)

5.3 wt.% magnesium stearate

6.0 wt.% BAYSILONETM oil M 100 (GE Bayer Silicones, viscosity 100 cSt (25°C))

5.3 wt.% SILWET™ L7607 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, methyl-terminated, molecular weight 1000 g/mol., viscosity 50 cSt (25°C)).

5 **Example 7**

5.3 wt.% magnesium stearate

6.0 wt.% BAYSILONE™ oil M 5 (GE Bayer Silicones, viscosity 5 cSt (25°C))

10 5.3 wt.% SILWET™ L77 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, methyl-terminated, molecular weight 600 g/mol., viscosity 20 cSt (25°C)).

Example 8

5.3 wt.% magnesium stearate

15 6.0 wt.% BAYSILONE™ oil M 5 (GE Bayer Silicones, viscosity 5 cSt (25°C))

5.3 wt.% SILWET™ L7608 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, hydrogen-terminated, molecular weight 600 g/mol., viscosity 35 cSt (25°C)).

20 **Example 9 (comparison)**

5.3 wt.% magnesium stearate

6.0 wt.% BAYSILONE™ oil M 100 (GE Bayer Silicones, viscosity 100 cSt (25°C))

25 5.3 wt.% SILWET™ L7608 (Crompton Specialities GmbH; ethoxylated polydimethylsiloxane, hydrogen-terminated, molecular weight 600 g/mol., viscosity 35 cSt (25°C)).

Table 2

Tabular comparison of the homogeneity of stock formulations:

| Example numbers | Homogeneity after preparation | Homogeneity after 24h/25°C* | Homogeneity after 24h/50°C* |
|-----------------|----------------------------------|--------------------------------|--------------------------------|
| 4 | very good | very good | Very good |
| 5 | very good | very good | Very good |
| 6 (comparison) | phase separation | phase separation | Agglomeration |
| 7 | very good | very good | Very good |
| 8 | very good | very good | Very good |
| 9 (comparison) | phase separation | phase separation | Agglomeration |

*storage temperature of the stock formulations.

As the Examples show, the homogeneity of the stock formulations is highly dependent on the viscosity of the polydimethylsiloxanes used. Phase separation occurs and the homogeneity of the stock formulations is lost if a more highly viscous polydimethylsiloxane is used with BAYSILONETM oil M100. In such stock formulations, agglomerates even form at a storage temperature of 50°C, as is conventional in the preparation of polyurethane urea compositions for the production of polyurethane urea fibers. In the production of polyurethane urea fibers, the formation of agglomerates leads to a reduction in the effectiveness of magnesium stearate as an agent for adjusting the adhesion, to a level of adhesion which changes over the duration of the spinning process, and to shortened filter useful lives. Accordingly, owing to the agglomerates, it is not possible to establish constant textile fiber data (adhesion) during the continuous production of polyurethane urea fibers. At the same time, the productivity of the spinning process is reduced.